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## (54) Drilling fluids and methods of using them

(57) A naphthenic oil is used as the oil component of an oil based drilling fluid that is used for carrying out of a subsea bore hole debris that may then be dumped in the sea while still contaminated with the oil.

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## **SPECIFICATION** Drilling fluids and methods of using them

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Drilling fluids are used to carry debris, such as drill cuttings, out of a bore hole during the drilling of the hole or during other operations within the hole. Thus the fluids are circulated down the hole and 5 carry the debris up the hole. Throughout this specification we use the term "drilling fluids" in the generic sense to mean the fluids (sometimes called muds) that are intended to be used during the actual drilling of an oil well or other bore hole as well as the fluids that are intended to be used at other stages, for instance the work over or completion of a well, such other fluids sometimes being known as

The debris that is carried from the bore hole by the drilling fluids is separated from the fluid at 10 work over fluids or packer fluids.

the head of the hole and the fluid is recycled. The debris may be dumped. The drilling fluids consist of a liquid phase and often contain also a solid phase dispersed in it, for instance a weighting agent such as barytes. The liquid phase may consist of water in which various minor additions may be dissolved or dispersed, e.g. various gelling agents and dispersing agents. 15 However it is often found that best results are obtained, especially during drilling, when the liquid phase includes oil, the fluids then being referred to as oil based drilling muds or fluids. Thus the liquid phase may consist of oil or it may be a mixture of oil and water, for instance an oil-in-water emulsion or

Numerous oils have been proposed for use as the oil in the liquid phase of drilling muds. There 20 have been some proposals to use vegetable or other edible oils but mineral oils have generally been a water-in-oil emulsion. 20 considered as more satisfactory and cost effective. Various mineral oils have been proposed. A typical disclosure is in British Petent Specification No. 1,487,841 in which it is stated that the oil may be diesel oil, crude oil, kerosene or other aliphatic hydrocarbons or mixtures. Another appears in US Patent Specification No. 2,969,321 in which the proposed oils are topped crude oils, gas oils, kerosene, diesel 25 fuels, heavy alkylates and fractions of heavy alkylates. Despite all these numerous proposals the oil was 25 generally chosen having regard primarily to availability and cost effectiveness and as a result the oil

that is used in practice is generally diesel oil. Despite the actual use of diesel oil in practice there are some examples in the literature of particular oils other than diesel oils. For instance various asphaltic, paraffinic and naphthenic oils are 30 exemplified in US Patent Specification No. 2,698,833 and in US Patent Specification No. 3,840,460 30 there is an example of an oil base that is a blend of sulphurised lard oil, chlorinated paraffin and a naphthenic mineral oil. The oils exemplified in US Patent 2,698,833 generally appear unsatisfactory by todays safety standards because of their generally low flash points and the oil exemplified in US Patent 3,840,460 suffers from the cost and other disadvantages incurred in the use of oils other than mineral 35 oils.

When the drill cuttings or other debris are separated from the drilling fluid, e.g. at the well head, the resultant separated debris will still be contaminated with the fluid phase of the drilling mud, and therefore with the oil if it is an oil based drilling mud. When the drilling is at sea the further treatment of the contaminated debris can create a problem. If the contaminating oil is toxic to marine life and the 40 40 contaminated debris is simply dumped into the sea then this dumping contaminates the sea unacceptably. Diesel oil has been shown to be toxic to marine life and so debris contaminated with diesel oil has to be washed before dumping but this requires extra apparatus on the rig or drilling platform and results in the generation of washings contaminated with oil, which in turn then have to be separated or treated further before they can be discharged. 45

In U.S. Patent No. 3,594,317 the problems arising from the anti-pollution regulations concerning the use of oils in drilling muds are discussed and it is stated that it has become necessary to find materials other than oil which will provide the attributes of oil in drilling mud. The proposal in that specification is to use decyl alcohol as a component of an aqueous based mud. Whilst this may avoid pollution problems decanol is not a satisfactory and cost effective alternative to oil in drilling muds, 50 especially in the more difficult bore holes where sticking of, for instance, the drill pipe is a particular

Recent tests in USA have indicated that the mineral seal oil available in USA from US refineries under the trade name Mentor 28 can be used in place of diesel oil as the oil in an oil based drilling fluid and that the resultant fluid is less toxic to marine life than fluids based on diesel oil. However Mentor 55 28 can be expensive and the toxicity of the fluids tested in USA still appears to be too high to be freely acceptable for dumping in the North Sea. Also it appears that the toxicity of the fluid may vary according to the source from which the Mentor 28 is obtained, and this renders it impracticable as a base for non-toxic drilling fluids. Another problem is that Mentor 28 is rather more viscous than diesel

According to the invention we have now surprisingly found that naphthenic oils are, as a class, especially suitable for use as the oil of oil based drilling fluids intended for carrying debris out of a subsea bore hole, prior to dumping of the debris in the sea while still contaminated with the oil. 60 Naphthenic oils may be derived from naphthenic crude and it seems that they can be much less

toxic to marine life than diesel oil and US Mentor 28. The naphthenic oil may be obtained by blending

Company and Clairsoi 350 supplied by Carless Solvents of Hackney Wick, London. Typically analyses

of these oils are as follows.

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		60 Solvent Pale	KL5	5	
	<del>-</del>	30.2	32.2		
	Gravity A.P.I. at 15°C	0.875	0.864		
	Density g/cm <sup>3</sup> at 15°C	145°C	142°C		_
	Flash Point — closed cup	_57°C	_54°C		5
5	Pour Point	24	15		
	Colour (Sabolt)	7.7	6.6		
	Viscosity cSt at 40°C	22.1	1.92.0		
	Viscosity cSt at 100°C	275°C	294°C		40
	Distillation — Initial Boiling Point	350°C	329°C (9	<b>5%</b> )	10
10	Final Boiling Point	76°C	80°C		
	Aniline Point	0.1-0.2%	less than	0.1	
	Sulphur Content	48.2%	53.9%		
	Paraffinic Content	48.5%	42.2%		
	Naphthenic Content	3.2%	3.9%		15
15	Aromatic Content (ASTM D2140)	11.6	11.5		
	Characterisation Factor	11.0	• • • •		
		POL	Y-X-HP36		
		<u></u>	20	_	
	Colour, Saybolt		860		20
	Density at 20°C	6			20
20	Kinematic Viscosity at 20°C cSt	3.	R		
	Kinematic Viscosity at 40°C cSt	1.			
	Viscosity at 100°C cSt	•	15		
	Flash Point (PMCC) °C		66		25
	Pour Point °C	2.			25
25	Sulphur Content %		1±1°C		
	Aniline Point		<b>%</b>		
	Aromatic Content Atoms		4%		
	Naphthenic Carbon Atoms Paraffinic Carbon Atoms	4	0%		
	r diamino Suissimo		Clairs	nol 350	30
30		Typical pr		Test method	
		i ypicai pi			-
		Good			
	Odour	Water W	hite		
	Colour	2.3 cSt			35
	Viscosity at 20°C	0.788		ASTM D1298	•
35	Density at 15°C			ASTM D 86	
	Distillation Range °C	200			
	Initial Boiling Point	221			
	50% Distils at	248			40
	Dry Point	74		ASTM D93	
40	Flash Point °C	28		ASTM D1133	
	Kauri Butanol Value	0.2%		CSL 808-4	
	Aromatic Content v/v	0.6		_	
	Low Explosive Limit (% volume in air)	7.1			45
	Upper Explosive Limit (% volume in air)	230			
45	Autoignition Temperature C	40% v/\	,		
	Naphthenic content	20% v/\			
	isoparaffin content	40% v/\			
	n_naraffinic content	200	-	by calculation	
	Threshold Limit Value (TLV) ppm	200			
				for Instance	a

Other oils having similar analysis may be used especially other naphthenic solvents, for instance having characteristics similar to Clairsol 350.

Any of these oils can be used individually or blends can be formed of two or more of these oils or of one or more of these oils with another oil, for instance a paraffinic oil. A suitable blend is formed of 40 to 90, preferably 60 to 80, parts by volume of a naphthenic oil with a paraffinic oil, provided the blend still has a sufficiently high naphthenic content to be classed as a naphthenic oil.

Diena still has a sumcientry high napromenic content to be classed as a napromenic on.

A suitable oil for use in the invention is formulated by blending 70 parts by volume of 60 Solvent Pale oil and 30 parts by volume of Clairsol 350. The resultant blended naphthenic oil has the following properties.

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		Typical properties	
	Aniline Point Flash Point	75.4°C 96°C –50°C	
5	Pour Point below Viscosity at 40°C Distillation range — Initial boiling point 10% boiling 50% boiling	4.19 cSt 214°C 236°C 292°C 320°C	5
10	90% boiling Final boiling point Estimated aromatic content Specific gravity	335°C 2.37% 0.849	10

A characteristic of the defined oils is that, compared to the toxicity of diesel oil, they are substantially non-toxic if they are dumped in the sea in relatively small quantities, e.g. as contamination on cuttings that have been separated from drilling fluid. Toxicity can be observed by determinining the effect of a selected amount of the oil in sea water on brown shrimps (*Crangon crangon*). Healthy shrimps are maintained in aerated sea water at 15°C in the presence of a selected concentration of the oil and the mortality of the shrimps after varying periods is observed. On this test diesel oil gives high oil and the mortality of the shrimps after varying periods is observed. On this test diesel oil gives high mortality, e.g. above 50% and often 90 to 100% at a concentration of 100 μ/l after 24 hours. The oils used in the invention preferably give substantially no mortality (for instance below 10% and preferably below 1%) at 24 hours when present in amounts of 100 μ/l and preferably also substantially no mortality when used in amounts of 333 μ/l for 24 hours. Preferably the mortality at 96 hours at 100 mortality when used in amounts of 333 μ/l for 24 hours. Preferably below 15% and preferably also the mortality μ/l is also low, generally below 30% and preferably below 15%. Generally the toxicity is such at 333 μ/l at 96 hours is in the same range, most preferably below 15%. Generally the toxicity is such that at least 50% of the brown shrimps survive for at least 5 days at oil concentrations of at least 333 μ/l and often of at least 1000 μ/l. A typical diesel oil, No. 2 diesel oil, results in only 50% survival after as little as 5.6 hours at a concentration of 100 μ/l.

The oil base of the drilling fluid may consist of the described mineral oil or it may be a blend of the described mineral oil and water. At least 1% by volume of this blend must be the mineral oil and generally the amount of oil is at least 30% by volume based on water plus oil, with the amount preferably being from 51 to 99%, most preferably 60 to 95% by volume oil, with the balance to 100% by volume being water. Depending upon the emulsifiers present and the amounts of oil and water the fluid may be a water-in-oil emulsion or an oil-in-water emulsion.

The water used for forming the fluid may be fresh water or sea water and may contain dissolved salts such as sodium chloride or calcium chloride, up to saturation concentrations. Thus the fluid may salts such as sodium chloride or calcium chloride, up to saturation concentrations. Thus the fluid may be an oil-in-water emulsion in which the water is a sodium chloride brine. An advantage of the use of the defined oils is that emulsions formed from them tend to be more stable than the corresponding emulsions formed from other, relatively non-toxic, mineral oils such as various paraffinic oils.

The drilling fluids may contain other additives as is conventional in oil based drilling fluids and these additives may be dissolved or dispersed in the oil base. Thus they may contain one or more emulsifiers, for instance, polymerised organic acids such as the product sold by the Applicant under the Trade Name Carbotec L and oil soluble amide polymers that are wetting agents and supplementary emulsifiers, such as the product sold by the applicant under the Trade Name Carbo-Mul. The amount of any emulsifiers is generally from 0.1 to 10% (of the commercial emulsifier) by volume, most preferably 1 to 5% by volume, based on the total volume of oil and water, or 1 to 20%, preferably 2 to 5% based on the water.

on the water.

The mud may contain high molecular weight organic polymers and inorganic bridging agents, such as the mixtures sold by the Applicants under the Trade Name Carbo-Trol. Lime hydrate may be dissolved in the water.

The drilling fluids will, in particular, generally contain a large amount of weighting material, such as barite, iron oxide, siderite or calcite. The amount of weighting aid is generally from 100 to 400 grams per 100 cc drilling fluids, for instance 200 to 500 pounds per barrel.

It is standard practice to adjust the rheological properties of oil based and other drilling fluids by including gelling agents in them. A variety of materials have been proposed as gelling agents. The most widely used gelling agents are bentonites, for instance the material commercially available as DMB (drilling mud bentonite) and the products available as Sedapol 155 or Sedapol 44, or Claytone 34 or Claytone 40. They can be used in the invention but better results are obtained by use of an organophilic hectorite.

This may be a naturally occurring hectorite or synthetic hectorite, for instance as described in British Patent Specification No. 1054111. If it is a synthetic hectorite it preferably includes exchangeable organic ammonium cations as described in British Patent Specification No. 1121501.

The preferred materials may be described as tetraalkylammonium hectorites, as described in British Patent Specification No. 1121501. One to three of the alkyl groups are preferably short chain

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alkyl groups (e.g. C<sub>1-8</sub> most preferably C<sub>1-9</sub>, typically methyl) and one to three of the alkyl groups are preferably long chain alkyl groups (e.g. C<sub>10-25</sub>, typically C<sub>14-22</sub>, most preferably C<sub>16</sub>).

A preferred material is dimethyldioctadecyl ammonium hectorite, preferably Bentone 38 or

Imvitone 1 or imvitone 2, which are derivatives of naturally occurring hectorite.

The amount of gelling aid is typically from 1 to 10, most preferably 1.25 to 4, grams gelling aid per 100 cc fluid. An alternative way of expressing the amount is as 3 to 15, most preferably 5 to 9, pounds gelling aid per barrel drilling fluid. In general the amount of gelling aid required in the fluids of the invention is greater than the amount required in conventional drilling fluids, for instance being from 1.5 to 2.5 times the amount required when the oil is diesel oil.

The following are examples of the invention.

A drilling fluid is prepared containing 212 cc Pale Qil 60 as defined above, 7 cc blown tall oil Example 1 emulsifier, 5 cc oil soluble amide polymer as secondary emulsifier, 53 cc water containing 25% calcium chloride, 6 g lime hydrate, 7 g of a blend of high molecular weight organic polymers and 15 inorganic bridging agents, 358 g barite and 6 g dimethyldioctadecyl ammonium hectorite.

Its properties are measured before and after hot rolling at 122°C for 17 hours (H/R). The results are set out in the following table. ES is electrical stability.

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20	Mud No. Mud Welght Flow Prop. Test temp °C Fann Readings rpm 600	1 14.5 49 223 128	H/R 14.5 49 226 130	H/R 14.5 65 125 71	20
25	300 200 100 6 3	95 59 16 14	94 55 13 10	52 32 9 8 54	25
30	Plastic Viscosity cp Yield point g/100 cm <sup>2</sup> Gel strength g/100 cm <sup>2</sup> E.S. volts at 49°C	95 16 8/12.5 1430	96 17 6/11.5 1160	8 4/7.5	30

When the oil was tested for toxicity by the method described above, it was found that after 96 hours it caused about 3% fatality at 333  $\mu$ VI and up to 15% fatality after 120 hours. In the same tests number 2 Diesel oil gives 93% fatality after 24 hours and 100% fatality after 72 hours at 100  $\mu$ VI, and the paraffinic oil sold as Mentor 28 gives about 59% fatality after 96 hours at 333  $\mu$ l/l.

35 Example 2

A drilling fluid is prepared having the same composition as above except that the amount of Pale Oil 60 is 149 cc and this is blended with 63 cc Clairsol 350. Very satisfactory downhole and toxicity properties are obtained when used in a subsea bore hole followed by filtration of the debris from the fluid and dumping of the debris in sea.

40 Example 3

A drilling fluid is prepared as in Example 1 except that POLY-X-HP35 is used in place of the Pale Oil 60. The resultant fluid had particularly good properties under high downhole temperature conditions.

A drilling fluid was prepared by blending 235 cc Clairsol 350, 5 cc primary emulsifier, 5 cc 45 secondary emulsifier, 9 grams gelling aid, 42 cc calcium chloride brine, 5 grams lime, 15 grams bridging aid and 309 grams barytes. This drilling fluid is a 13 pound per gallon mud having an 85:15 oil:water ratio and an internal phase activity of 0.75. Its initial properties at 49°C were plastic viscosity 22 cps, yield point 5.5 g/100 cm² and gel strength 3/6.5 g/100 cm² and after hot rolling at 65°C were 50 plastic viscosity 23 cps, yield point 7 g/100 cm² and gel strength 5/6.5 g/100 cm². It is particularly 50 suitable for use in subsea drilling where the sea temperature may be 5°C or lower.

A drilling fluid is prepared as in Example 2 using a bentonite gelling aid in place of the hectorite. The resultant fluid is less satisfactory when it is allowed to cool to, say, 5°C but still gives useful 55 downhole properties.

It should be noted that best results are obtained when the oil has an aromatic content of below 15, and preferably below 5 and most preferably below 1% by volume when measured by ASTM 2007 (especially when the oil is a naphthenic solvent) or, if it is an insulating oil, when its aromatic content is

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1. A method in which an oil based drilling fluid is used to carry debris out of a subsea bore hole Claims 5 and the debris is then dumped in the sea while contaminated with the fluid, in which method the oil of the oil base is a naphthenic oil.

2. A method according to claim 1 in which the oil has a naphthene content of 30 to 70%.

3. A method according to claim 1 or claim 2 in which the oil is derived from a naphthenic crude. 4. A method according to claim 1 or claim 2 in which the oil is a blend of an oil derived from a 10

naphthenic crude with a paraffinic oil. 5. A method according to any preceding claim in which the oil contains not more than 5%

aromatic compounds.

6. A method according to any preceding claim in which the oil contains not more than 2.5% 15 15 aromatic compounds. 7. A method according to any preceding claim in which the oil has a viscosity at 40°C of less than

6 cSt 8. A method according to any preceding claim in which the oil has a viscosity at 20°C less than

10 cSt. 9. A method according to any preceding claim in which the oil has a viscosity at 40°C of from 1 20 20 to 5.5 cSt and at 20°C of from 1 to 7 cSt and at 100°C of from 0.7 to 2.5 cSt.

10. A method according to any preceding claim in which the oil is less viscous at 20°C than

11. A method according to any preceding claim in which the oil is selected from 60 Solvent Pale, 25 KL55, POLY-X-HP35 and Clairsol 350 and oils having substantially the same properties as any of 25 these, and blends of two or more such oils.

12. A method according to any preceding claim in which the oil gives a mortality of brown shrimps of below 5% when tested in serated sea water at 15°C for 24 hours at a concentration of 333

13. A method according to any preceding claim in which the oil is substantially free of benzopyrene and 1,2,5,6-dibenzanthracene and other polynuclear toxic aromatic compounds.

14. A method according to any preceding claim in which the oil base consists of 30 to 100% by volume of the naphthenic oil and 70 to 0% water and the drilling fluid also includes drilling fluid additives selected from gelling agents, emulsifiers, bridging agents, weighting agents and lime.

15. A method according to any preceding claim substantially as herein described with reference 35. to any of the examples.

16. An oil for use as the oil in an oil based drilling fluid and which is a naphthenic oil.

17. An oil for use as the oil in an oil based drilling fluid for carrying out of a subsea bore hole debris that is then dumped in the sea, and in which the oil is a naphthenic oil.

18. An oil according to claim 16 or claim 17 and which is as defined in any of claims 2 to 13. 19. An oil according to claim 16 or claim 17 substantially as herein described with reference to

any of the examples. 20. An oil based drilling fluid in which the oil of the oil base is a naphthenic oil.

21. An oil based drilling fluid for carrying out of a subsea bore hole debris that is then dumped in 45 the sea and in which the oil of the oil base is a naphthenic oil.

22. A drilling fluid according to claim 20 or claim 21 and which is as defined in any of claims 2 to

14. 23. A drilling fluid according to claim 20 or claim 21 substantially as herein described with reference to any of the examples.